“Half-lanthanidocenes catalysts via the ”borohydride/alkyl” route: A simple approach of ligand screening for the controlled polymerization of styrene.”

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Half-lanthanidocenes catalysts via the "borohydride/alkyl" route: A simple approach of ligand screening for the controlled polymerization of styrene.

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Summary

The "borohydride/alkyl" (B/A) route initially reported for isoprene has been applied successfully to the polymerization of styrene. This method provides via an *in situ* approach an interesting tool for the assessment of the influence of a ligand on the performance of half-lanthanidocene catalysts. All systems lead to well controlled oligomerization / polymerization processes. This method is thus a convenient tool for the controlled polymerization of styrene starting from a common trisborohydride precursor and commercial ligands. The influence of the nature of several ligands on the activity could be established, with trends corresponding to those obtained starting from the isolated precursors: HCp ~ HCp^{Ph3} > HCp* (Cp=C_5H_5, Cp^{Ph3}=1,2,4 $Ph_3C_5H_2$, Cp*=C_5Me_5). These results suggest an influence of the electron donating ability of the ligand rather than steric requirements.

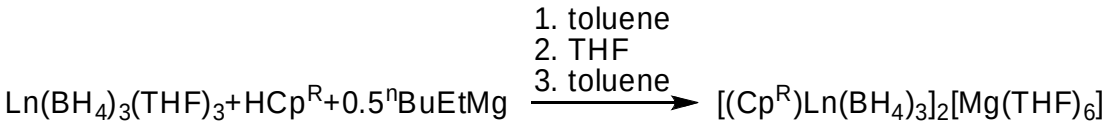
Résumé

La voie borohydrure/alkyl initialement développée pour la polymérisation de l'isoprène a été appliquée avec succès à la polymérisation du styrène. Cette méthode utilisée selon une approche *in situ* se révèle être un outil intéressant pour évaluer l'influence d'un ligand sur les performances catalytiques de complexes de type hemi-lanthanidocènes. Tous les systèmes générés par cette voie conduisent à une oligomérisation / polymérisation du styrène bien contrôlée. Cette approche constitue donc une méthode simple pour polymériser le styrène de manière contrôlée à partir d'un précurseur trisborohydrure et de ligands commerciaux. L'influence de la nature d'un ligand sur l'activité de a pu être établie : HCp ~ HCp^{Ph3} > HCp*. Ces résultats suggèrent une influence de la densité électronique des ligands plutôt que de facteurs stériques.

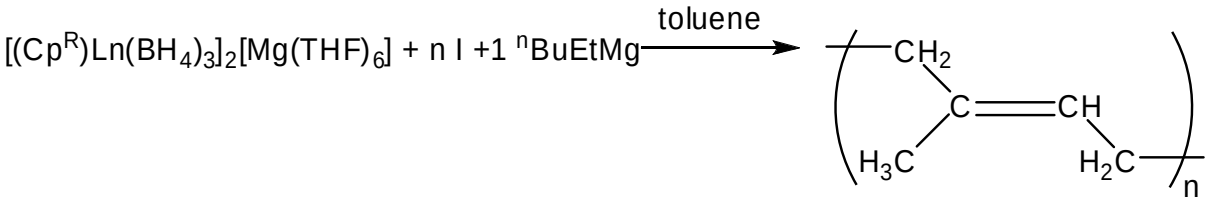
1. Introduction

Rare earth half-sandwich complexes are known as highly versatile polymerization precatalysts or catalysts. A $Cp^*La[CH(SiMe_3)_2]_2$ ($Cp^* = C_5Me_5$) half-lanthanocene was reported for the polymerization of various polar and non-polar monomers in a controlled fashion [1]. Cationic systems based on a $(C_5Me_4SiMe_3)Sc(CH_2SiMe_3)_2(THF)$ half-scandocene were reported for the polymerization and copolymerization of various non-polar monomers, leading notably to unprecedented styrene-ethylene copolymers that incorporate syndiotactic sequences [2]. Another example is given by a $Cp^*Nd(BH_4)_2(THF)_2$ borohydrido half-neodymocene that leads after an *in situ* alkylation to new stereoregular block [3] and statistical [4] isoprene-styrene copolymers and to the unprecedented polystyrene catalyzed chain growth on a metal [3]. Despite such promising potentialities, polymerization catalysis using mono(cyclopentadienyl) complexes of the rare earths remains poorly explored in comparison to their metallocene homologues, probably due to the difficulties encountered in the synthesis of these compounds. Indeed, rare earth half-sandwich complexes are generally considered as poorly stable, electronically more unsaturated and sterically opened in comparison with lanthanidocenes, and as a consequence, elaborated synthetic routes have to be used [5]. We developed recently a simple and convenient route toward the formation of borohydrido half-lanthanidocenes, where the cyclopendadienyl ligand is introduced from its neutral protonated form using an alkylmagnesium reagent associated to a trisborohydride precursor [6]. The so called "borohydride/alkyl route" lead on one hand to a new family of bimetallic ionic compounds of the general formula $[(Cp^R)Ln(BH_4)_3]_2[Mg(THF)_6]$ ($Cp^R = Cp^* = C_5Me_5$, Ln = Nd, **1a**, Ln = La, **1b**; $Cp^R = Cp = C_5H_5$, Ln = Nd, **2a**; $Cp^R = Cp^{Ph3} = C_5H_2Ph_3$, Ln = Nd, **3a**) that could be isolated using a one-pot synthesis (Scheme 1, [7]). Combined to dialkylmagnesium, their application to the polymerization of isoprene reveals a highly stereoselective reaction (Scheme 2).

Scheme 1. B/A synthesis of the ionic compound.



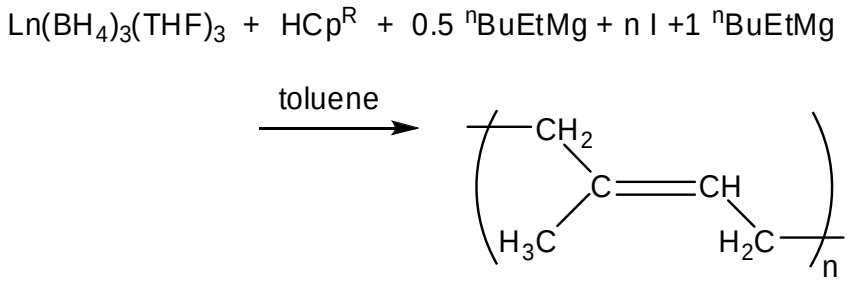
Scheme 2. Polymerization involving the ionic compound obtained by the B/A route (I=isoprene).



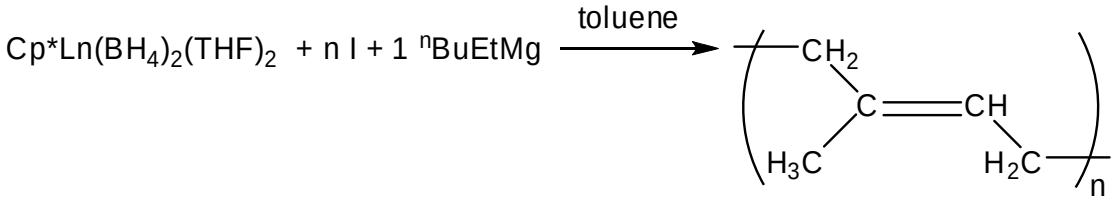
We performed on the other hand the polymerization using an *in situ* generated monoCp neodymium active species by the B/A route in the presence of isoprene and using an additional equivalent of dialkylmagnesium for the alkylation step (Scheme 3). The resulting catalytic properties were similar not only to those observed starting from the isolated bimetallic complex **1a**, but also to those starting from of the neutral homologue $Cp^*Nd(BH_4)_2(THF)_2$ (Scheme 4, [6]) obtained by ionic metathesis. This *in situ* one pot method enables thus to generate very easily sophisticated catalytic systems that are obtained after several synthetic steps, and to evaluate the influence of specific ligands on the catalytic behaviour of half-lanthanidocenes in a simple and convenient way. We report in this frame, after a brief extension to the polymerization of isoprene using lanthanum based half-sandwiches, a similar strategy applied to the polymerization of styrene. Reactions performed via this B/A route with *in situ* introduction of the ligand starting from HCp*, HCp and HCp^{Ph3}

ligands are confronted to the polymerization mediated by the complexes **1a, 1b, 2a** and **3a**[a]. It is shown that the former method enables not only to evaluate the effect of a ligand on the catalytic properties in a simple way, but leads also to a well controlled polymerization of styrene starting from a common trisborohydride precursor combined to commercial ligands and dialkylmagnesium compound.

Scheme 3 Polymerization by B/A *in situ* route (I = isoprene).



Scheme 4 "Regular" poylmerization starting from the neutral half-lanthanidocene (I = isoprene).



[a] We distinguish the B/A *in situ* route represented Scheme 3, where the ligand is introduced in its protonated form in the polymerization medium from the B/A route starting from the half-lanthanidocene ionic precursors **1a**, **1b**, **2a** and **3a** where the ligand is introduced from the coordination sphere of the metal in the polymerization medium (Scheme 2)

2. Half-lanthanocenes for the polymerization of isoprene

The polymerization of isoprene using complex $[(Cp^*)La(BH_4)_3]_2[Mg(THF)_6]$ **1b** combined to *n*-butylethylmagnesium is reported Table 1, together with the results obtained according to the B/A *in situ* monoCp generation depicted on Scheme 3. Both entries can be compared to the polymerization of isoprene using the trisborohydride precursor $La(BH_4)_3(THF)_3$ **4b** combined to *n*-butylethylmagnesium [8]**.** The introduction of the pentamethylcyclopentadienyl ligand using the B/A routes leads to (i) a significant increase of the activity, from 1 to 20 kg/mol/h, (ii) an increase of the *trans*-selectivity of the reaction, from *ca.* 93 to 97% and (iii) narrower molecular weight distributions (entries 1 and 2 vs. [8]). Both routes involving a monoCp compound lead to similar activity and selectivity, following the trends observed for neodymium based compounds [6]. The B/A *in situ* route is thus a convenient tool to evaluate the role played by the ligand, even if the resulting molecular weights are slightly less controlled (PDI = 1.63 vs. 1.39 for entry 2 and 1, respectively).

Table 1

Polymerization of isoprene using the lanthanum bimetallic ionic precatalyst **1b** and comparison with the *in situ* generation of the active species

Entry	Precatalyst	Time (h)	Yield (%)	Activity kg/mol/h	$\overline{M_n}$ th[c] g/mol	$\overline{M_n}$ [d] g/mol	PDI[e]	1,4-trans (%)[(f)]	1,4-cis (%)[(f)]	3,4 (%)[(f)]
1[a]	**1b**	2	60	20.4	39900	43100	1.39	97.6	0.5	1.9
2[b]	*(In situ)*	2	58	19.6	39200	25300	1.63	96.7	0.3	3
[8][a]	**4b**	24	25	0.7	17200	17300	1.84	92.8	5.3	1.9

[a] Reactions conducted at 50°C with 10^{-6} mol of **1b** or **4b**, 1 equivalent *n*-butylethylmagnesium for the alkylation and a I/La ratio of 1000 in 1 mL toluene (I = isoprene)

[b] Reactions conducted at 50°C with 10^{-6} mol of **4b**, 1 equivalent HCp*, 1.5 equivalent *n*-butylethylmagnesium and a I/La ratio of 1000 in 1 mL toluene (Scheme 3)

[c] Expected molecular weight assuming one growing chain per lanthanum: $\overline{M_n}_{th}$ = yield%*[I]/[A]

[d] Number-average molecular weight measured by SEC

[e] Polydispersity index measured by SEC (PDI = $\overline{M_w}/\overline{M_n}$)

[f] Determined by ^{1}H NMR

3. Half-lanthanidocenes for the polymerization of styrene

3.1 Polymerization starting from ionic bimetallic precatalysts

The polymerization of styrene using complexes **1a**, **1b**, **2a**, and **3a** combined to *n*-butylethylmagnesium according to Scheme 2 is reported in Table 2. All systems are able to oligomerize / polymerize styrene at 50 °C. The introduction of the pentamethylcyclopentadienyl ligand using this B/A route leads to (i) a decrease in activity and (ii) narrower molecular weight distributions as compared to the trisborohydride precursors $Ln(BH_4)_3(THF)_3$ (Ln = Nd, **4a** and Ln = La, **4b**). For neodymium based catalysts, molecular weights are smaller than expected considering two growing chains per magnesium atom[b], highlighting possible uncontrolled transfer reactions. If the polydispersity is acceptable (PDI< 1.3) in the first steps of the polymerization, the molecular weight broadens along the polymerization for higher St/Ln ratios, probably as a consequence of the advanced transfer reactions. The lanthanum based system leads in turn to a controlled polymerization of styrene independently of the St/Ln ratio (PDI = 1.22) with an activity similar to that of its neodymium homologue. Concerning the ligand effect, a slightly higher activity after 2h (entries 7 and 9 *vs.* 3) can be observed using Cp and Cp^{Ph3} vs. Cp*, which suggests an influence of the electron donating ability rather than steric requirements. ^{13}C NMR spectra in the phenyl *ipso* carbon region were found to be in agreement with a syndiotactic-rich polystyrene[c], independently of the nature of the ligand. A representative pattern is given Figure 1e.

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[b] Molecular weight distributions resulting from the polymerization of styrene using the neutral $Cp^*Nd(BH_4)_2(THF)_2$ compound combined to *n*-butylethylmagnesium are consistent with the growth of one macromolecular chain per alkyl group, see ref. [3].

[c] From ^{13}C NMR spectra (Figure 1), the syndiotacticity of the corresponding polymers did not enable to distinguish the four heptads characteristics of highly syndiotactic polystyrene [9] and to perform a quantitative analysis.

Table 2

Polymerization of styrene using bimetallic ionic precatalysts

Entry [a]	Complex (Ln, ligand)	St/Ln	Time (h)	Yield (%)	Activity kg/mol/h	$\overline{M_n}$ th[b] g/mol	$\overline{M_n}$ [c] g/mol	PDI[d]
3	**1a** (Nd, Cp*)	100	2	24	1.2	1200	650	1.14
[10]	**4a**	100	2	58	3.0	3000	2700	1.7
4	**1a** (Nd, Cp*)	429	20	45	1.0	10000	7200	1.81
5	**1b** (La, Cp*)	100	2	18	0.9	900	640	1.22
[10]	**4b**	100	2	78	4.0	4100	6000	1.7
6	**1b** (La, Cp*)	440	20	45	1.0	10300	13100	1.22
7	**2a** (Nd, Cp)	100	2	26	1.4	1400	720	1.26
8	**2a** (Nd, Cp)	456	20	42	1.0	10000	3500	2.28
9	**3a** (Nd, Cp^{φ}_3)	100	2	30	1.6	1600	730	1.32
10	**3a** (Nd, Cp^{φ}_3)	435	20	39	0.9	8800	3400	2.52

[a] Reactions conducted at 50°C with 0.5 mL styrene in 0.5 mL toluene in combination with *n*-butylethylmagnesium

[b] Expected molecular weight assuming two growing chains per magnesium atom: $\overline{M_n}_{th}$ = yield%*[St]/2[Mg] (St = styrene)

[c] Number-average molecular weight measured by SEC

[d] Polydispersity index measured by SEC (PDI = $\overline{M_w}/\overline{M_n}$)

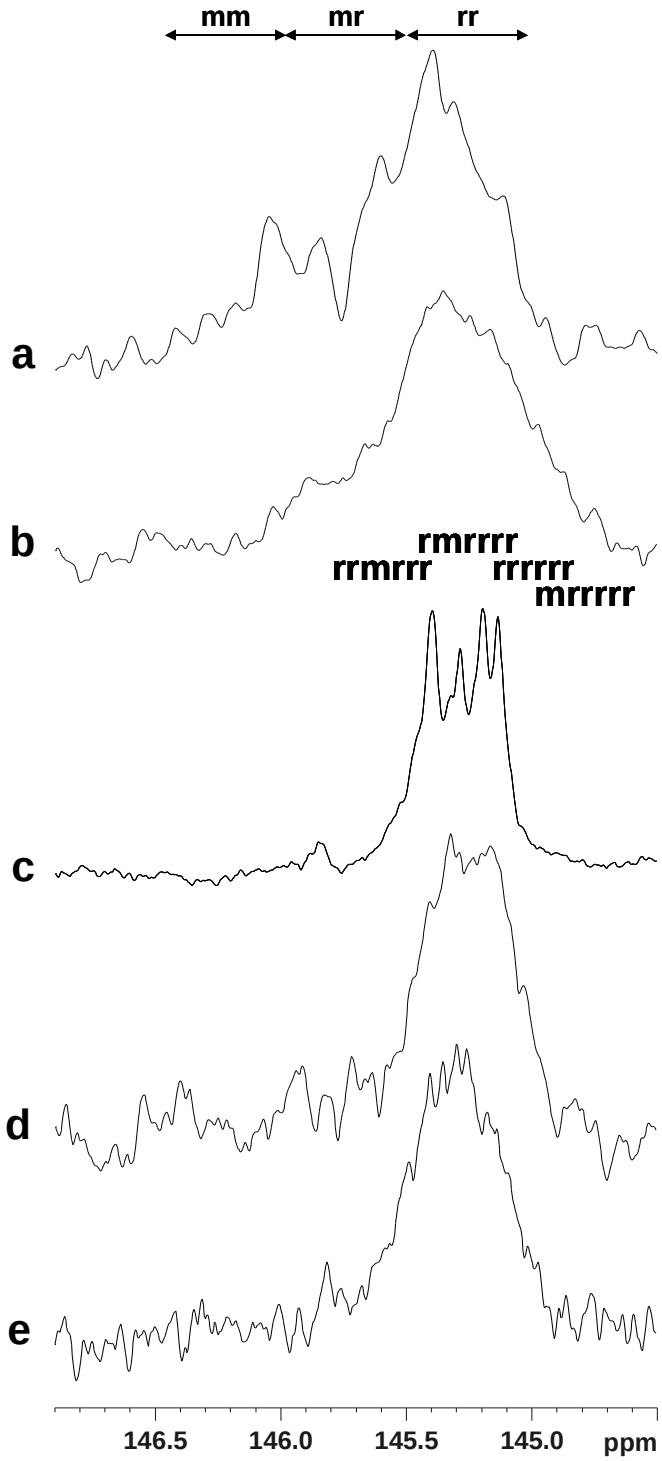


Fig. 1. ^{13}C NMR spectra in the phenyl *ipso* carbon region for atactic polystyrene resulting from an AIBN initiated radical polymerization (a), for a $Nd(BH_4)_3(THF)_3$ – *n*-butylethylmagnesium combination (b), for a $Cp^*Nd(BH_4)_2(THF)_2$ – *n*-butylethylmagnesium combination, for entry 14 (d) and for entry 10 (e).

3.2 Polymerization following the B/A in situ *pathway*

The polymerization of styrene according to Scheme 3 starting from HCp*, HCp and HCp^{Ph3} is reported in Table 3. From the value of the polydispersity indexes (PDI ≤ 1.25 except for HCp^{Ph3} for a St/Nd ratio of 440), all systems are able to oligomerize / polymerize styrene with a well controlled character at 50 °C. The introduction of a cyclopentadienyl ligand, particularly HCp* using the "borohydride/alkyl" *in situ* route leads to (i) a decrease in activity and (ii) narrower molecular weight distributions as compared to the trisborohydride precursors **4a** and **4b.** It is notewoethy that the PDI remains in the controlled range for higher St/Nd ratio and longer polymerization times (except for HCp^{Ph3}) as opposed to the broadening observed starting from the ionic precursor. The reaction leads moreover to a syndiotactic-rich polystyrene, independently of the nature of the ligand. A representative pattern is given Figure 1d. A higher activity after 2h is observed using HCp and $HCp^{\varphi}{}_3$ vs. HCp*, which confirms the trends observed previously. From entry 16, a good agreement between experimental and calculated number-average molecular weight is observed with HCp combined to neodymium trisborohydride.

Table 3

Polymerization of styrene – B/A *in-situ* generation of monoCp complexes

Entry [a]	Ln	Ligand	St/Ln	Time (h)	Yield (%)	Activity kg/mol/h	$\overline{M_n}$ th[b] g/mol	$\overline{M_n}$ [c] g/mol	PDI[d]
11	Nd	HCp*	100	2	19	1	1000	470	1.19
[10]	Nd	-	100	2	58	3.0	3000	2700	1.7
12	Nd	HCp*	440	20	27	0.6	6400	8900	1.14
13	La	HCp*	100	2	20	1	1000	500	1.19
[10]	La	-	100	2	78	4.0	4100	6000	1.7
14	La	HCp*	433	20	22	0.5	5000	7700	1.09
15	Nd	HCp	100	2	33	1.7	1700	1000	1.20
16	Nd	HCp	440	20	68	1.6	15500	15700	1.25
17	Nd	HCp^{Ph3}	100	2	26	1.4	1400	800	1.16
18	Nd	HCp^{Ph3}	440	20	37	0.8	8500	3750	1.75

[a] Reactions conducted at 50°C with 0.5 ml styrene in 0.5 ml toluene in combination with *n*-butylethylmagnesium

[b] Expected molecular weight assuming two growing chains per magnesium atom: $\overline{M_n}_{th}$ = yield%*[St]/2[Mg] (St = styrene)

[c] Number-average molecular weight measured by SEC

[d] Polydispersity index measured by SEC (PDI = $\overline{M_w}/\overline{M_n}$)

3.3 Comparison with the neutral precatalyst

The polymerization of styrene using the neutral compound $Cp^*Nd(BH_4)_2(THF)_2$ [3] vs. the ones obtained from the B/A route (ionic and *in situ* introduction of the ligand) is reported Table 4. The activities observed are higher and the control over the molecular weight is better using the neutral half-neodymocene: the number-average molecular weights are closer to the theoretical ones considering two growing chains per magnesium atom. In contrast to the pathway involving the ionic bimetallic precatalyst, and in a similar way to the B/A *in situ* route, the polydispersity remains constant along the polymerization and for higher St/Nd ratios. The selectivity is higher using the neutral compound, as it is possible to quantitate the syndiotacticity (around 85%) from the heptads observed on the ^{13}C NMR pattern (Figure 1c, [3]).

Table 4

B/A generated vs. neutral precatalysts

Entry [a]	Route	St/Nd	Time (h)	Conversion (%)	Activity kg/mol/h	$\overline{M_n}$ calc.[b] (g/mol)	$\overline{M_n}$ [c] (g/mol)	PDI [d]
3	Ionic	100	2	24	1.2	1200	650	1.14
11	*(In situ)*	100	2	19	1	1000	470	1.19
[3]	Neutral	100	2	31	1.6	1600	1400	1.32
4	Ionic	429	20	45	1.0	10000	7200	1.81
12	*(In situ)*	440	20	27	0.6	6400	8900	1.14
[3]	Neutral	440	20	81	1.9	18500	16000	1.22

[a] Reactions conducted at 50°C with 0.5 ml styrene in 0.5 ml toluene in combination with *n*-butylethylmagnesium

[b] Expected molecular weight assuming two growing chains per magnesium atom: $\overline{M_n}_{th}$ = yield%*[St]/2[Mg] (St = styrene)

[c] Number-average molecular weight measured by SEC

[d] Polydispersity index measured by SEC (PDI = $\overline{M_w}/\overline{M_n}$)

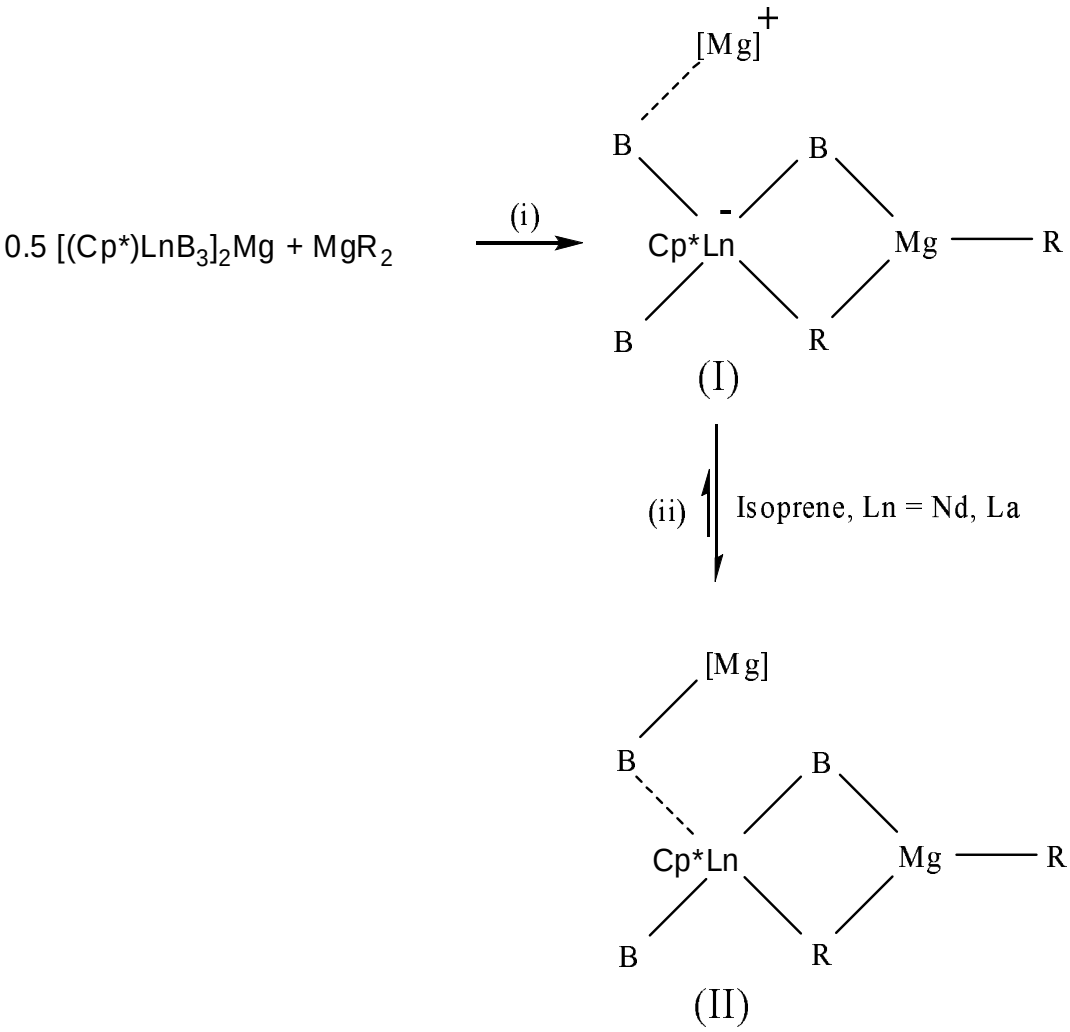
4. Discussion

The extension of the B/A strategy, initially developed for the neodymium mediated polymerization of isoprene, to the lanthanum based polymerization of isoprene has been carried out successfully. The B/A approach has been further applied to the half-lanthanidocene mediated polymerization of styrene. Trends for activity and selectivity obtained using the *in situ* strategy were found to be in agreement with those observed starting from the isolated ionic half-lanthanide complexes: similar activities for Nd vs. La based catalytic systems, a smaller activity for HCp* vs. HCp and HCp^{Ph3}, and syndiotactic-rich polystyrenes. This confirms the usefulness of such an approach for evaluating the influence of a ligand onto the catalytic properties. The B/A *in situ* route leads moreover to narrow molecular weight distributions ($1.09 < PDI < 1.25$ except for HCp^{Ph3} and a St/Nd ratio of 440): one can thus consider this strategy as a very simple way to polymerize styrene in a controlled fashion starting from a common trisborohydride precursor and a commercial ligand. Such behaviour is however not observed starting from the neodymium based ionic precursors **1a**, **2a** and **3a**, where a broadening is observed for higher St/Nd ratios and longer times. Such a broadening is, interestingly, not observed with the lanthanum compound **1b**.

The similar behaviour of the routes involving neutral or ionic monoCp precatalysts observed in the course of the neodymium mediated polymerization of isoprene was explained on the basis of a dissociation of the ionic complex releasing a BH_4^- group, leading to the same active species as that of the neutral compound [6]. The possible steps leading to this active species involving two borohydrido groups per metal atom is represented Scheme 5. Such a dissociation of the ionic form, that occurs in the presence of *n*-butylethylmagnesium, would thus not occur in the presence of the bulky and less coordinating styrene in the case of neodymium based catalysts since the results are different (*vide infra*). As a consequence, the active species may have the form of a crowded complex involving three BH_4 per metal

analogue to (I) in Scheme 5, leading to a poorer control over the molecular weight along the polymerization. A "putative active species" in the presence of an additional [Mg]B ligand may also be considered. A possible explanation is that such active species simply favours an uncontrolled transfer reaction as compared to the "neutral" active species. The weaker Lewis

Scheme 5. Dissociation of the ionic precatalysts after addition of (i) one equivalent dialkylmagnesium and (ii) isoprene in excess. B represents a BH_4 group, and THF molecules are omitted for clarity.



acidity of the lanthanum element may in turn render this dissociation possible in a styrene surrounding, and lead to an active species that enables a good control of the polymerization[d]. The smaller activity and selectivity observed for neodymium based B/A approaches vs. the neutral one may be related to the presence of higher quantity of THF in the medium [6], and possibly to the additional BH_4^- group in the coordination sphere of the metal. This BH_4^- group may increase the electron density which would result in a more difficult coordination of styrene.

The results from this study acts finally toward the existence of different active species for the polymerization of styrene following the different routes, in contrast to isoprene: this can be related to previous findings showing important differences between the polymerization of isoprene and that of styrene using half-lanthanidocenes combined to dialkylmagnesium : two growing chains per magnesium atom are observed for styrene using $Cp^*Nd(BH_4)_2(THF)_2$ combined to *n*-butylethylmagnesium [3], whereas only one in the case of isoprene [8]. Fast and reversible transfer reactions could moreover been achieved in the case of styrene [3], while an excess of magnesium decreases the activity and broadens the molecular weight distribution of the resulting polyisoprene [8].

5. Conclusion

The "borohydride/alkyl" route has been applied successfully to the polymerization of styrene. When the ligand is introduced *in situ*, this method provides an interesting tool for the assessment of the influence of a ligand on the performance of half-lanthanidocene catalysts. All systems tested via this approach lead to well controlled oligomerization / polymerization processes (PDI < 1.2 in most cases). This highlight a simple way to polymerise styrene in a controlled fashion starting from a common trisborohydride precursor combined to a

[d] The exact nature of the active species involved in the half-lanthanidocene / dialkylmagnesium mediated polymerization of styrene is still the subject of investigation in our group.

commercial ligand HCp^R. The influence of the nature of a ligand on the activity of borohydrido based catalytic systems could be established, with trends corresponding to those obtained starting from the isolated ionic precursors $[(Cp^R)Ln(BH_4)_3]_2[Mg(THF)_6]$: HCp ~ HCp^{Ph3} > HCp*. Those results suggest an influence of the electron donating ability rather than steric requirements.

6. Experimental section

6.1 Materials

All operations were performed under dry argon by using Schlenk techniques. Toluene was dried over sodium / benzophenone and distilled over molecular sieves before use. Styrene and isoprene (99% from Aldrich) were dried over calcium hydride and distilled over molecular sieves. *n*-butylethylmagnesium (from Texas Alkyl) and di-*n*-hexylmagnesium (from Akzo Nobel) were both used as 20% wt. solutions in heptane. $Ln(BH_4)_3(THF)_3$ [11] and $[(Cp^R)Ln(BH_4)_3]_2[Mg(THF)_6]$ [7] complexes were synthesized according to literature procedure.

6.2 Polymerisation

6.2.1 Ionic precatalysts.

In a glove box, the borohydrido complex was weighed into a vessel. Toluene, styrene and *n*-butylethylmagnesium were added in the flask in this order using syringes. The mixture was magnetically stirred at the reaction temperature for a given time, diluted in toluene and the resulting solution was poured into ethanol, leading to the precipitation of an off-white polymer. Solvents were evaporated under partial vacuum, and the product was dried under vacuum for 48h.

6.2.2 In situ introduction of the ligand.

In a glove box, the borohydrido complex was weighed into a vessel. Ligand, ½ equivalent of *n*-butylethylmagnesium, toluene, styrene and 1 equivalent *n*-butylethylmagnesium were added in the flask in this order using syringes. The same procedure as above was employed.

6.3 Measurements

^{1}H spectrum of polyisoprene was recorded on a AC 300 Bruker spectrometer at room temperature in $CDCl_3$. ^{13}C NMR spectra of the polystyrene were recorded on a AC 400 Bruker spectrometer at 380K and 400K in tetrachloroethane-*d2*. The chemical shifts were calibrated using the residual resonances of the solvent. Size exclusion chromatography (SEC) of polystyrenes was performed (i) in THF as eluent at 20°C using a Waters SIS HPLC-pump, a Waters 410 refractometer and Waters styragel column (HR2, HR3, HR4, HR5E) for soluble low molecular weight oligomers resulting from polymerizations conducted with a St/Ln ratio of 100 and (ii) in trichlorobenzene as eluent at 135°C using a Waters 150C PLUS device with coupled refractometer and viscosity detectors for the other experiments. The number-average molecular weight and polydispersity index were calculated using polystyrene standards.

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